1922
M92

TELLURIUM ALLOYS

BY

LOTTIE ELLA MUNN
A. B. Baldwin Wallace College, 1917

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1922

URBANA, ILLINOIS

1922
M92

UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

May 22, 1922

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY LOTTIE ELLA MUNN

ENTITLED TELLURIUM ALLOYS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science

R. S. Hopkins
In Charge of Thesis

W. A. Noyes
Head of Department

Recommendation concurred in*

Committee on Final Examination*

*Required for doctor's degree but not for master's

499066

Table of Contents.

I.	Introduction	1.
II.	Experimental Work	6.
III.	Results	9.
IV.	Attempt to Analyze Lead-Tellurium Mixtures	14.
V.	Summary	16.
VI.	Bibliography	17.
VII.	Acknowledgment	18.

Digitized by the Internet Archive
in 2015

https://archive.org/details/telluriumalloys00munn

I. INTRODUCTION.

The element tellurium is not so rare as is generally supposed.[1] A recent estimate of the amount of tellurium that the United States can produce, without making any material additions to present plants, is 125,000 lbs. annually.[2,3,4] There is little market for tellurium and a corresponding small production, only one or two refineries reporting production or sale of the element. Tellurium, like selenium, is a by-product of the electrolytic refining of copper. The domestic production is capable of large expansion if market conditions should warrant, as almost all blister copper contains recoverable quantities of tellurium. Much of this would be saved, if a demand existed, at prices of $1.50 to $2.50 per lb. In 1917, prices at the refinery averaged $3.00 per lb., but a very small additional output would probably have flooded the market.

The chemical characteristics of tellurium are much like those of sulfur, but as would be expected in an element of higher atomic weight, it is more metallic. Tellurium looks much like antimony. It is silver-white and so crystalline that it is quite brittle and can be powdered. Toward acids it is as refractory as antimony; toward alkaline solutions it is strongly resistant, while in water or moist air it does not rust or corrode appreciably. A consideration of these properties led to the idea that tellurium might be used as an alloying material to make metals more resistive to corrosion.

Although the literature on the subject reveals the preparation of several tellurium alloys, no studies have been

made as to their corrosion resisting power.(5) Pushin prepared several alloys by fusing together weighed amounts of the pure metals under a layer of potassium chloride and lithium chloride (to prevent oxidation), and pouring the melt into molds of chalk or magnesium oxide. The alloys of silver and tellurium were black, crystalline, harder than either component, but very brittle. The properties of the copper-tellurium alloys varied greatly with composition. When rich in copper, they were dark gray, crystalline, and brittle; with 30 to 33% tellurium they became much darker and more brittle; with more than 33% tellurium, they were violet in color, and with more than 50%, they were golden brown. Two compounds, Cu_2Te and CuTe, formed solid solutions with each other. Alloys with lead, containing 50% tellurium, were gray, granular, and brittle; PbTe formed solid solutions with lead but not with tellurium. Brittleness and a coarse grained structure also characterized the tin-tellurium alloys. The investigator proved the existence of the compounds Ag_2Te, Cu_2Te, PbTe, and SnTe.

(6) Two Japanese scientists, Chikashige and Nose, give give reports of work done on aluminium-tellurium alloys. Since tellurium and aluminium unite with explosive violencewhen heated together, the tellurium was first fused in a porcelain tube and the aluminium gradually added. Two compounds were formed, Te_3Al_2, and Te_3Al_5. Te_3Al_2, which melted at 895°, formed solid solutions with tellurium up to 4.4% tellurium. The two compounds were rapidly decomposed by water, and evolved a disagreeable poisonous gas H_2Te, which rapidly decomposed into tellurium and hydrogen.

(7) Henry Fay found that tin and tellurium united to form a compound SnTe, which melted at 769°. This compound formed

with tellurium a eutectic which melted at 399°, and consisted of 85% tellurium and 15% tin. With tin the compound also formed a eutectic, but the solution of SnTe in tin was so low that it was impossible to locate the concentration. The melting point of the eutectic of low concentration appeared to be the same as that of pure tin.

(8) J. K. Rose has established a complete freezing point curve for varying concentrations of gold and tellurium. The curve showed one compound $AuTe_2$, with a melting point of 452°. This compound formed a eutectic with tellurium, containing 20% gold and melting at 397°; with gold it formed a eutectic containing 60% gold, melting at 432°.

(9) Kimata states that only one compound of antimony and tellurium exists, the formula being Sb_2Te_3 and the melting point 620°. This compound formed with antimony a eutectic melting at 540° and containing 27-28% tellurium; and with tellurium a eutectic melting at 420°, containing a little under 90% tellurium.

(10) The melting point curves worked out by H. Pelabon showed the existence of Sb_2Te_3(m.p.600°), SnTe(m.p.780°), Bi_2Te_3(m.p.583°), PbTe(m.p.860°), AgTe(m.p.955°), and Au_2Te_4(m.p. 472°).

(11) Ransom and Thieme conceived the idea that tellurium might be used as a hardener for lead and other metals. When pure lead was melted and tellurium sprinkled on it, the tellurium glowed, and large lumps were formed, mixed with a coarse powder which floated as a dross. Upon separating the lumps from the powder the former were found to be hard, somewhat malleable, and to contain both lead and tellurium. Tellurium could not be found in the

yellow powder and its nature has not been established. Some pure tin bars were melted and poured, and after removing from the heat tellurium was added in powder form and stirred in. No glowing was observed but a dross appeared on the surface. The alloy contained 1.12% tellurium, was slightly harder than pure tin, and the tensile strength had increased from 3800 to 4265 lbs. per sq. in. Similar experiments were performed with zinc and aluminium, but only traces of tellurium were found in the treated metal, most of it being in the dross; however the tensile strength was increased from 4955 to 5510 lbs. per sq. in. in the case of zinc, and from 13840 to 14810 lbs. per sq. in. for aluminium. The hardness was not changed.

(12)

Fay and Gillson have also made investigations with regard to lead-tellurium alloys. The composition of the alloy of maximum freezing point corresponds with the proportions of the metals in PbTe. Lead easily became supersaturated with PbTe, which separated out at the higher freezing point, and the lower freezing point then corresponded to the solidification of lead. When still more tellurium was present, PbTe again separated at the higher temperature, but the lower freezing point corresponded with the complete solidification of the alloy, which was a eutectic of PbTe and tellurium. When examined microscopically the eutectic could be seen interspersed between the crystals of lead or tellurium, according to which was present in excess. Alloys containing more than 50% tellurium were very brittle.

This sums up very briefly the greater part of the work which has been done along this line. The resistance of tellurium to the action of acids and alkalies led to the present

investigation as to the corrosion of lead-tellurium alloys, with the hope that the addition of a small percentage of tellurium would make the lead more resistive to corrosion, without making it too brittle for its ordinary uses.

II. Experimental Work.

Since the brittleness of the lead-tellurium alloy increases rapidly with increase in the percentage of tellurium, no attempt was made to use more than 10% of the latter, a 10% alloy being too brittle to serve the purposes for which lead is ordinarily used. The amounts of lead and tellurium, corresponding to the various percentages of tellurium desired, were carefully weighed out into clay crucibles and thoroughly mixed. On account of the ease with which tellurium volatilizes and oxidizes, the mixture was then covered with a layer of charcoal before fusion. A gas furnace furnished a sufficiently high temperature for the fusion, since the melting points of lead and tellurium are respectively 327^{0} and 451^{0}. After fusion for twenty minutes, the mixture was allowed to cool and the charcoal was removed from the top; sufficient heat was then applied to melt the alloy, so that it could be poured into a graphite mold, forming strips of fairly uniform surface. The mold consisted of two plates of graphite, clamped tightly together; on the inner surface of one of them a rectangular depression about two and one half inches long, three-fourths of an inch wide, and one-eigth of an inch deep had been cut by a chisel. Some difficulty was experienced in getting a smooth surface on the strips containing the higher percentages of tellurium. This was overcome by sandpapering.

For the corrosion tests, the alloys were first weighed and then placed in nitric acid (.01 and .1 molal), also in hydrochloric acid (.1 molal), and in sulfuric acid (.1 molal)

for successive periods of five days each. After each period the strips were removed, cleaned, dried, and weighed before replacing in the acids on the shaking machine. The shaking machine served to agitate the solutions sufficiently so that they should not form saturated layers around the alloys. From the loss in weight, the per cent of corrosion was calculated. The greatest difficulty encountered in these tests was to remove the corrosion completely or at least equally from the strips, especially in the case of the .01 molal nitric acid, where a yellowish-white precipitate always formed and clung tenaciously to the surface. This precipitate upon analysis seemed to contain no tellurium, and was probably a basic nitrate of lead, which formed due to the great dilution of the nitric acid. Best results were obtained by simply removing the corrosion by means of a brush, except in the case of the sulfuric acid, where it was necessary to place the strips in sodium acetate solution for equal lengths of time in order to remove the lead sulfate. In all probability this difficulty in removal of corroded material caused the discrepancies which will be seen in the results. However, since in general the relationships were the same between successive five day periods, fairly representative results were obtained by averaging the percentages of corrosion, and plotting these averages against the composition.

No curve is shown for the results with sulfuric acid because the values obtained were very irregular. This is due no doubt, as said before, to the very slight action of sulfuric acid on lead and to the unequal removal of corrosion. The curve for .01 molal nitric worked out well and showed an increased re-

sistance with increase of tellurium present. Some irregularities are seen in the curves for .1 molal nitric acid and .1 molal hydrochloric acid, especially in the case of the former, where there is a very marked increase in corrosion for alloys containing .07% and .09% of tellurium. This is probably due to experimental error but it is possible that another compound of lead and tellurium is formed. In general, the presence of tellurium seems to lessen the corrosion to a slight extent.

III. RESULTS.

Per cent of Corrosion in .01 Molal HNO_3.

	1.	2.	3.	4.	5.	6.	7.	8.	Av.
Pb	1.0376	1.0000	1.1880	1.0397	0.9999	0.9895	0.9995	1.0395	1.0367
1%Te	0.7794	0.6648	0.7760	0.6322	0.7118	0.9137	0.8984	0.9566	0.7919
2%Te	0.8102	0.5828	0.7751	0.6513	0.7443	0.8239	0.8958	0.9550	0.7798
3%Te	0.5965	0.4365	0.5702	0.5923	0.7313	0.6875	0.7040	0.6817	0.6250

Per cent of corrosion in .1 Molal HNO_3.

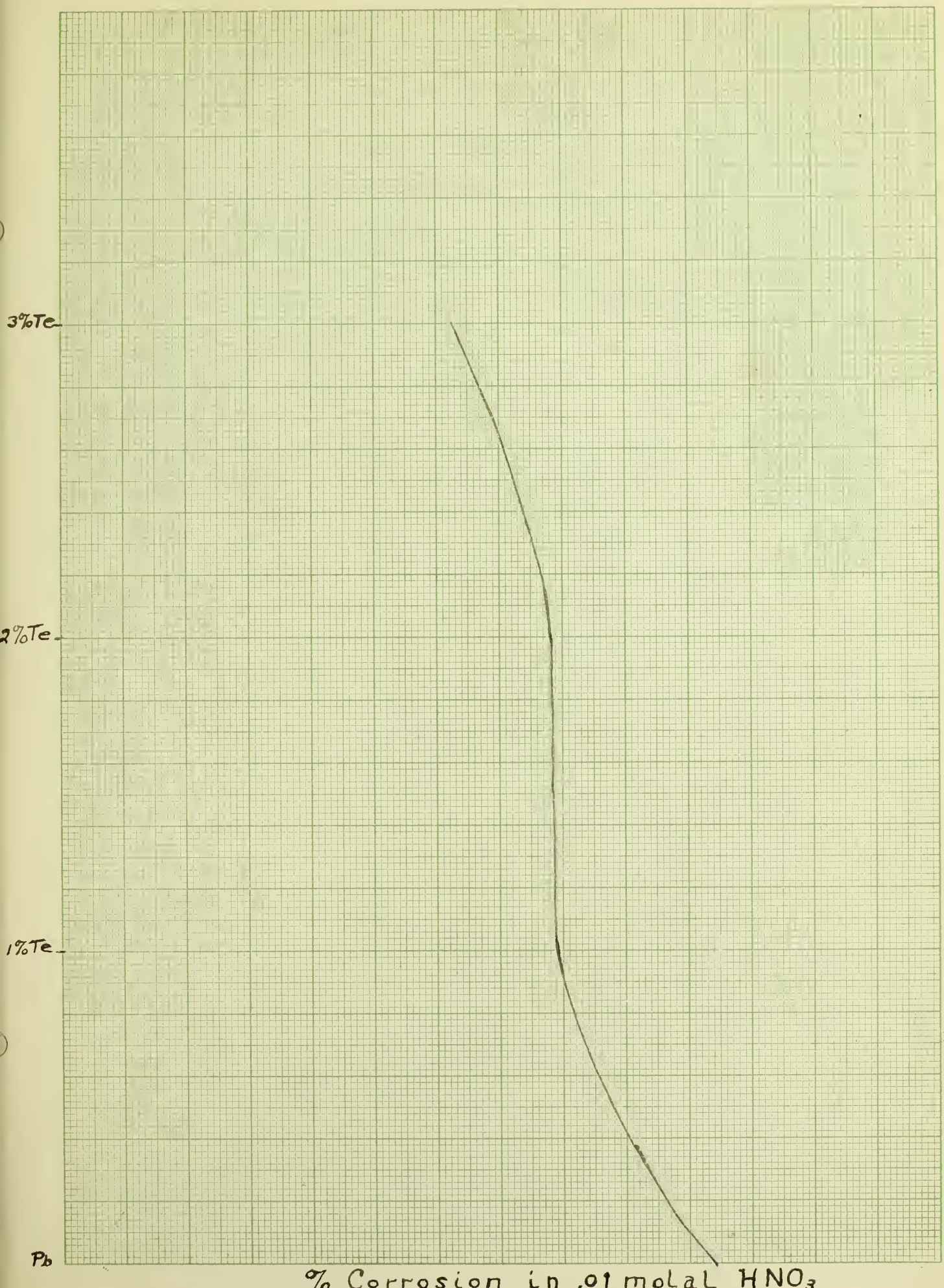
	1.	2.	3.	4.	5.	6.	Av.
Pb	1.3220	2.0549	1.6117	1.6363	1.6944	2.3291	1.7744
.06%Te	1.0400	1.9161	1.4355	1.5804	1.7842	2.2569	1.6688
.07%Te	2.4290	2.9415	3.2776	3.1406	3.2975	3.5813	3.1112
.09%Te	2.5000	2.6105	2.9663	3.0241	3.2492	3.2956	2.9409
.10%Te	1.2790	2.5608	1.4111	1.2947	1.7881	2.0616	1.7325
.30%Te	1.3000	2.6582	1.5834	1.5620	1.6139	1.9704	1.7708
.50%Te	1.2110	2.6463	1.5200	1.6163	1.5488	2.0132	1.7592
.80%Te		1.6920	1.3639	1.5950	1.6837	2.5569	1.7783
1%Te		1.6629	1.3398	1.3528	1.8245	2.2585	1.6877
2.2%Te		1.6511	1.3943	1.4443	1.9058	2.1360	1.7063
5%Te	1.7840	2,2813	1.8191	1.7641	2.3293	2.7045	2.1137
8%Te	2.1550	2.9483	2.0399	2.1373	2.7031	3.2356	2.5382
10%Te	3.1780	3.2662	2.3101	2.0669	2.9671	3.8926	2.7775

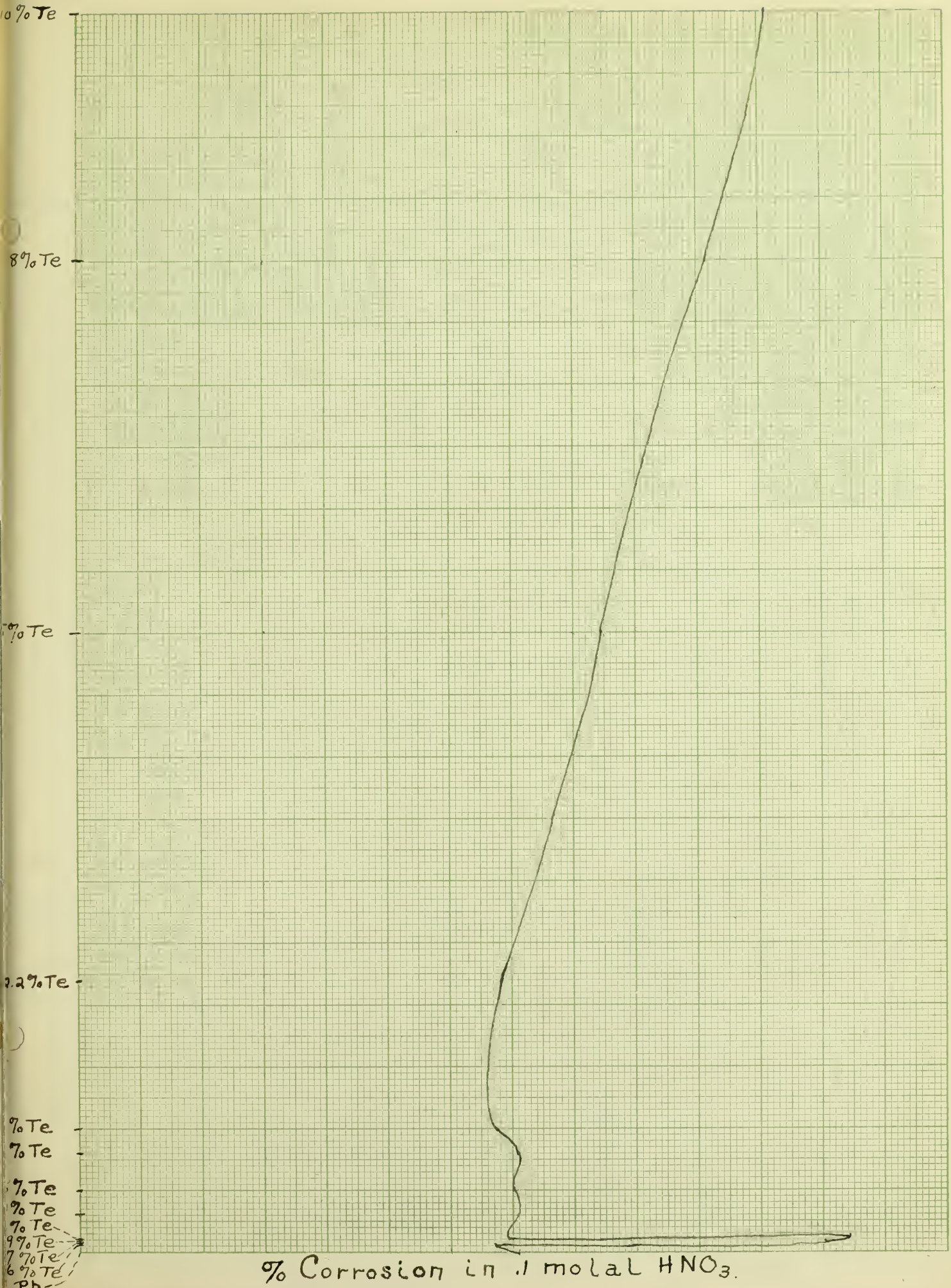
Per cent of corrosion in .1 Molal HCl.

	1.	2.	3.	4.	5.	Av.
Pb	0.1001	0.5924	0.5881	0.7277	0.5638	0.5144
.06%Te	0.0931	0.4024	0.5613	0.5764	0.5254	0.4317
.07%Te	0.0993	0.4107	0.5397	0.5478	0.6255	0.4466
.20%Te	0.1342	0.4937	0.6030	0.6067	0.7006	0.5076
.40%Te	0.0621	0.3497	0.4901	0.5894	0.5302	0.4043
.80%Te	0.0982	0.4302	0.5062	0.5814	0.6010	0.4434
1.00%Te	0.0992	0.3932	0.5165	0.5241	0.5141	0.4094
2.20%Te	0.1225	0.4126	0.5457	0.6166	0.6231	0.4641
6.70%Te	0.1301	0.4525	0.6354	0.3438	0.7039	0.5531

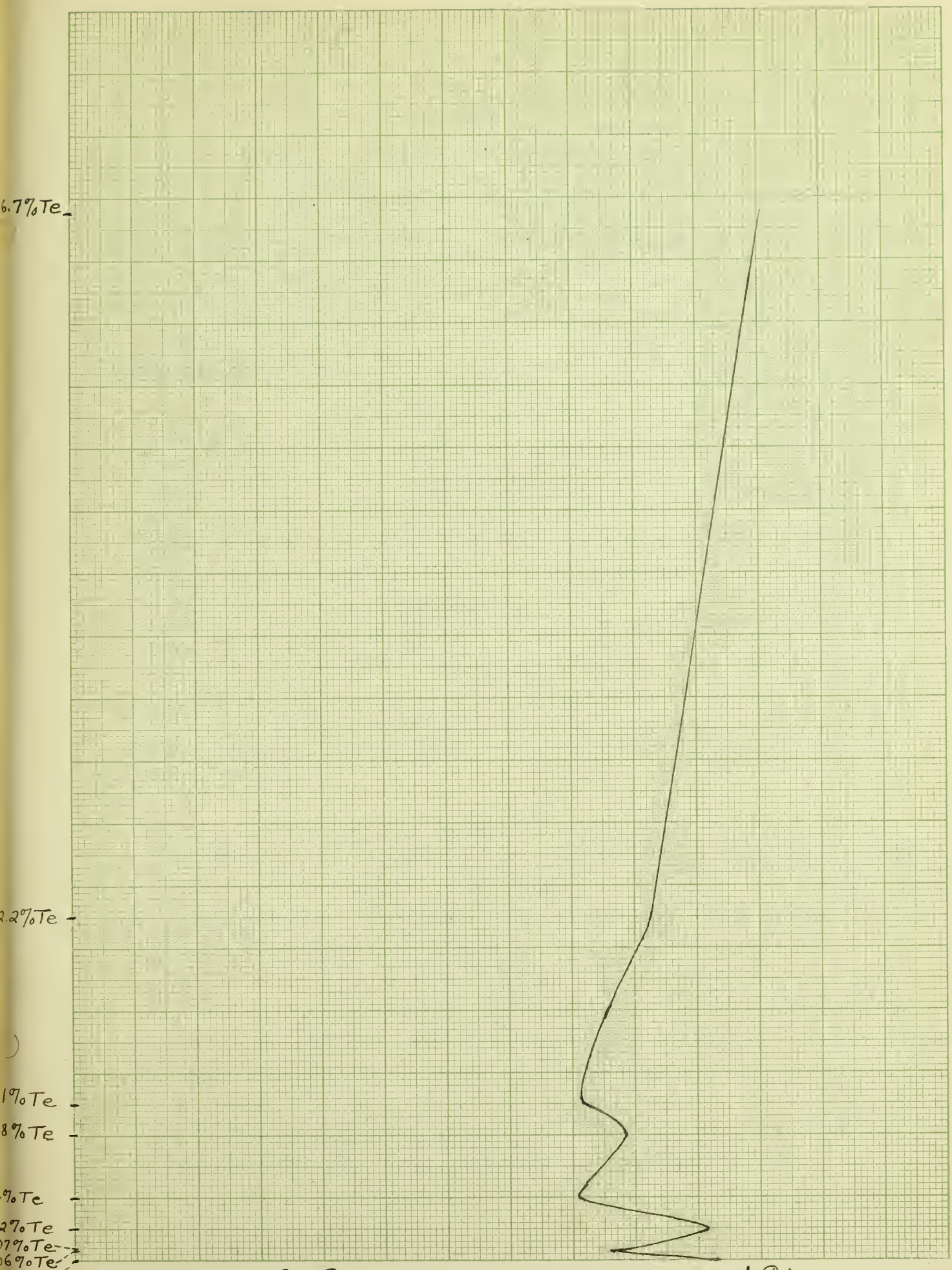
Per cent of corrosion in .1 Molal H_2SO_4.

	1.	2.	3.	4.	Av.
Pb	0.0116	0.0156	0.0058	0.0097	0.0107
.07%Te	0.0083	0.0264	0.0059	0.0177	0.0146
.20%Te	0.0069	0.0108	0.0000	0.0079	0.0064
.40%Te	0.0000	0.0099	0.0000	0.0119	0.0055
.80%Te	0.0184	0.0160	0.0100	0.0020	0.0116
1.00%Te	0.0000	0.0060	0.0040	0.0041	0.0035


3%Te
2%Te
1%Te
Pb
% Corrosion in .01 molal HNO_3.



% Corrosion in .1 molal HNO_3.



% Corrosion in .1molal HCL.

IV.

Attempt to Analyze a Lead-Tellurium Mixture.

The separation and quantitative determination of tellurium from a mixture of lead and tellurium presents several difficulties, such as the formation of lead tellurate, the volatility and oxidation of tellurium, occlusion of sulfur etc., depending upon the method used. The following methods were tried:

1. A mixture of lead and tellurium was evaporated just to dryness with nitric acid, forming lead nitrate and tellurium dioxide, which upon treatment with sodium hydroxide dissolved to form sodium plumbite and sodium tellurite. Hydrogen sulfide was then used to precipitate the lead as lead sulfide, the sodium tellurite remaining in solution. When the latter was acidified and hydrogen sulfide again passed in, the tellurium was precipitated as metallic tellurium, which was filtered off, evaporated to dryness with nitric acid, and ignited gently to tellurium dioxide.

$$\left.\begin{matrix}Pb\\Te\end{matrix}\right\}\xrightarrow{HNO_3}\left.\begin{matrix}Pb(NO_3)_2\\TeO_2\end{matrix}\right\}\xrightarrow{NaOH}\left.\begin{matrix}Na_2PbO_2\\Na_2TeO_3\end{matrix}\right\}\xrightarrow[H_2S]{PbS}Na_2TeO_3\xrightarrow{HCl,H_2S}\underline{Te}\xrightarrow{HNO_3}\underline{TeO_2}$$

The determination was not at all successful owing probably to the volatility of tellurium dioxide.

2. The procedure was carried out the same as in 1, as far as the separation and formation of tellurium dioxide. This was then dissolved in sodium hydroxide, forming sodium tellurite, oxidized to sodium tellurate by sodium peroxide, and precipitated as barium tellurate by the addition of barium chloride.

$$\left.\begin{matrix}Pb\\Te\end{matrix}\right\}\xrightarrow{HNO_3}\left.\begin{matrix}Pb(NO_3)_2\\TeO_2\end{matrix}\right\}\xrightarrow{NaOH}\left.\begin{matrix}Na_2PbO_2\\Na_2TeO_3\end{matrix}\right\}\xrightarrow{H_2S}\begin{matrix}\underline{PbS}\\Na_2TeO_3\end{matrix}\xrightarrow{HCl,H_2S}\underline{Te}$$

$$\underline{Te}\xrightarrow{HNO_3}\underline{TeO_2}\xrightarrow{NaOH,Na_2O_2}Na_2TeO_4\xrightarrow{BaCl_2}\underline{BaTeO_4}$$

The barium tellurate was ignited and weighed, but in every case the weight was much too high. This might be accounted for by the fact that there must be a large amount of sulfur precipitated with the tellurium, and this sulfur would be oxidized to a sulfate and be precipitated as barium sulfate along with the barium tellurate. The possibility of occlusion is also great. The use of hydrogen peroxide as an oxidizing agent gave the same results.

3. The method which promised to give the best results was the standard method of precipitation by sulfur dioxide in hydrochloric acid solution. The mixture of lead and tellurium was evaporated to dryness with nitric acid and the products dissolved in sodium hydroxide, forming sodium plumbite and sodium tellurite. Upon acidifying with hydrochloric acid, most of the lead precipitated as lead chloride and was filtered off. When sulfur dioxide was then passed into the solution, the tellurium came down as the element, and was filtered, dried, and weighed.

$$\left.\begin{matrix}Pb\\Te\end{matrix}\right\}\xrightarrow{HNO_3}\left.\begin{matrix}Pb(NO_3)_2\\TeO_2\end{matrix}\right\}\xrightarrow{NaOH}\left.\begin{matrix}Na_2PbO_2\\Na_2TeO_3\end{matrix}\right\}\xrightarrow{HCl}\begin{matrix}\underline{PbCl_2}\\H_2TeO_3\end{matrix}\xrightarrow{SO_2}\underline{Te}$$

V. Summary.

1. When exposed to the action of .01 molal nitric acid, alloys of lead and tellurium seem to show an increase of resistance to corrosion with increase of tellurium present.

2. Alloys of lead and tellurium containing from .06% to 5% tellurium, with the exception of the .07% and .09% alloys, show a slightly greater resistance to the action of .1 molal nitric acid than does lead.

3. Pure lead is corroded more by .1 molal hydrochloric acid than are its alloys with tellurium, containing up to 4.8% of the latter.

4. The results indicate that in general tellurium increases the resistance of lead to .1 molal sulfuric acid; however these results are very irregular and unreliable on account of unequal removal of corroded material.

5. Tellurium is probably best determined quantitatively by reduction to metallic tellurium by sulfur dioxide in hydrochloric acid solution, after filtering off the lead chloride. The tellurium is then dried and weighed.

VI. Bibliography.

1. Lenher,V.------ J. Ind. and Eng. Chem.,12,597-8.
2. Umpleby,J.B.------ Min. Res. of U.S.,1917.
3. Hill,J.M.------ U.S.Geol.Survey, 1918.
4. Loughlin,G.F. and Clark,Martha B.------ Min.Res. of U.S.,1919.
5. Pushin,N.A.------ J.Russ.Phys.Chem.Soc.,39,13-54.
6. Chikashige,M. and Nose,J.------ Mem.Coll.Sci.Kyoto Imp. Univ. 2,227-32.
7. Fay,Henry------ J.Am.Chem.Soc.,29,1265-8.
8. Rose,T.K.------ Trans.Inst.Min.Metal.Brit.,17,Pt.I,285-9.
9. Kimata,Y.------ J.Soc.Chem.Ind.,34,1211.
10. Pelabon,H.------Ann.Chem.Phys.,17,526-66.
11. Ransom,J.H. and Thieme,C.O.------ Chem.and Met.,25,102.
12. Fay,Henry and Gillson,C.B.------Amer.Chem.J.,27,81-95.

VII. Acknowledgment.

The writer hereby wishes to acknowledge her indebtedness and to extend her thanks to Dr. B.S.Hopkins, under whose direction this work was done.

UNIVERSITY OF ILLINOIS-URBANA
3 0112 108854354